

# Synthesis and reactivity of dichloroboryl complexes of platinum(II)

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The reaction between  $[\text{Pt}(\text{nbe})_3]$  (nbe = norbornene), two equivalents of the phosphines  $\text{PPh}_3$ ,  $\text{PMePh}_2$  or  $\text{PMe}_2\text{Ph}$  and 1 equivalent of  $\text{BCl}_3$  affords the platinum dichloroboryl species  $[\text{PtCl}(\text{BCl}_2)(\text{PPh}_3)_2]$ ,  $[\text{PtCl}(\text{BCl}_2)(\text{PMePh}_2)_2]$  and  $[\text{PtCl}(\text{BCl}_2)(\text{PMe}_2\text{Ph})_2]$ . All three complexes were characterised by X-ray crystallography and reveal that the boryl group lies *trans* to the chloride. With  $\text{PMe}_3$  as the phosphine, the complex  $[\text{PtCl}(\text{BCl}_2)(\text{PMe}_3)_2]$  is isolated in high yield as a white crystalline powder although crystals suitable for X-ray crystallography were not obtained. Crystals were obtained of a product shown by X-ray crystallography to be the unusual dinuclear species  $[\text{Pt}_2(\text{BCl}_2)_2(\text{PMe}_3)_4(\mu\text{-Cl})][\text{BCl}_4]$  which reveals an arrangement in which two square planar platinum(II) centres are linked by a single bridging chloride which is *trans* to a  $\text{BCl}_2$  group on each platinum centre. The reaction of  $[\text{PtCl}(\text{BCl}_2)(\text{PMe}_3)_2]$  with  $\text{NEt}_3$  or pyridine (py) affords the adducts  $[\text{PtCl}\{\text{BCl}_2(\text{NEt}_3)\}(\text{PMe}_3)_2]$  and  $[\text{PtCl}\{\text{BCl}_2(\text{py})\}(\text{PMe}_3)_2]$ , respectively, both characterised spectroscopically. The reaction between  $[\text{PtCl}(\text{BCl}_2)(\text{PMe}_3)_2]$  and either 4 equivalents of  $\text{NHEt}_3$  or piperidine (pipH) results in the mono-substituted boryl species  $[\text{PtCl}\{\text{BCl}(\text{NEt}_3)\}(\text{PMe}_3)_2]$  and  $[\text{PtCl}\{\text{BCl}(\text{pip})\}(\text{PMe}_3)_2]$ , respectively, the former characterised by X-ray crystallography. Treatment of either  $[\text{PtCl}(\text{BCl}_2)(\text{PMe}_3)_2]$  (in the presence of excess  $\text{NEt}_3$ ) or  $[\text{PtCl}\{\text{BCl}(\text{NEt}_3)\}(\text{PMe}_3)_2]$  with catechol affords the B(cat) (cat = catecholate) derivative  $[\text{PtCl}\{\text{B}(\text{cat})\}(\text{PMe}_3)_2]$  which is also formed in the reaction between  $[\text{Pt}(\text{PMe}_3)_4]$  and  $\text{ClB}(\text{cat})$  and also from the slow decomposition of  $[\text{Pt}\{\text{B}(\text{cat})\}_2(\text{PMe}_3)_2]$  in dichloromethane over a period of months. The compound  $[\text{Pt}\{\text{B}(\text{cat})\}_2(\text{PMe}_3)_2]$  was prepared from the reaction between  $[\text{Pt}(\text{PMe}_3)_4]$  and  $\text{B}_2(\text{cat})_2$ .

## Introduction

Transition metal boryl compounds<sup>1</sup> remain a focus of continued interest not least because of their involvement in various metal catalysed diboration and other borylation reactions.<sup>2</sup> In most examples, the boron of the boryl ligand is bonded to a single metal centre and two additional atoms which are usually good  $\pi$ -donors such as oxygen or nitrogen incorporated into diolato or amido groups respectively; the B(cat) group, where cat = catecholate, is one of the most studied.<sup>1</sup> More recent investigations, notably by Braunschweig *et al.* and Aldridge *et al.*, have focussed on more reactive boryl species in which the R groups of the  $\text{BR}_2$  ligand are hydrocarbyl and/or halogeno groups.

With particular reference to dihaloboryl ligands,  $\text{BX}_2$  (X = F, Cl, Br, I), the earliest examples were reported by Nöth and Schmid in the 1960's.<sup>3</sup> Thus in a series of papers, reviewed in ref. 3, these authors described a range of dichloroboryl species including  $[\text{Co}(\text{BCl}_2)(\text{CO})_3(\text{L})]$  (L = CO,  $\text{PPh}_3$ ,  $\text{AsPh}_3$ ),  $[\text{Mn}(\text{BCl}_2)(\text{CO})_4(\text{PPh}_3)]$ ,  $[\text{Fe}(\text{BCl}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  and  $[\text{Mo}(\text{BCl}_2)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  each derived from the reaction between  $\text{BCl}_3$  and the corresponding metal carbonylate anion. Alternatively, dihaloboryl species were reportedly formed *via* B–X bond (X = halide) oxidative addition to Pt(0) or Co(0) centres, examples being the Pt(II) species  $[\text{PtBr}(\text{BBr}_2)(\text{PPh}_3)_2]$  and the Co(II), formally 19-electron, complexes  $[\text{CoX}(\text{BX}_2)(\text{dppe})_2]$  (X = Cl, Br, I; dppe = 1,2-bis(diphenylphosphino)ethane),<sup>3,4</sup> both proposed to have a *cis* configuration. The bis-boryl, 19-electron Co(II) complexes *trans*- $[\text{Co}(\text{BX})_2(\text{dppe})_2]$  (X = Br, I) were also described,

derived from the reaction between  $[\text{CoH}(\text{dppe})_2]$  and  $\text{BX}_3$ .<sup>3,5</sup> These latter complexes were reported to be particularly versatile boryl transfer agents, the complex *trans*- $[\text{Co}(\text{BBr}_2)_2(\text{dppe})_2]$  being used to synthesise complexes of rhodium, copper and silver containing the  $\text{BBr}_2$  ligand.<sup>3,5</sup> Nevertheless, despite the impressive number of reports, none of these early compounds were structurally characterised and, partly on the basis of the <sup>11</sup>B NMR data presented, some doubt remains as to their correct formulation.

More recent work has provided the first definitive characterisation of dihaloboryl species. Thus, the first structurally characterised  $\text{BF}_2$  complexes *cis*- $[\text{Pt}(\text{BF}_2)_2(\text{PPh}_3)_2]$ ,  $[\text{Pt}(\text{BF}_2)_2(\text{dppb})]$  (dppb = 1,2-bis(diphenylphosphino)butane) and *fac*- $[\text{Ir}(\text{BF}_2)_3(\text{CO})(\text{PPh}_3)_2]$  were recently described by us derived from the oxidative addition of  $\text{B}_2\text{F}_4$  to Pt(0) and Ir(I) precursors respectively;<sup>6</sup> spectroscopic data for an iridium  $\text{BF}_2$  complex  $[\text{IrH}(\text{BF}_2)(\text{PMe}_3)(\eta\text{-C}_5\text{Me}_5)]$  had previously been reported by Bergman and co-workers.<sup>7</sup> In 2000, the osmium dichloroboryl complex  $[\text{OsCl}(\text{BCl}_2)(\text{CO})(\text{PPh}_3)_2]$  ( $\delta_{\text{B}}$  52.5) was described by Roper *et al.* having been prepared from the reaction between  $[\text{OsCl}(\text{Ph})(\text{CO})(\text{PPh}_3)_2]$  and  $\text{HBCl}_2 \cdot \text{Et}_2\text{O}$ .<sup>8</sup> This and a number of subsequent reports revealed a rich chemistry of the  $\text{BCl}_2$  ligand involving substitution at boron and resulting in a range of new boryl, tethered boryl and base-stabilised borylene complexes of osmium.<sup>8,9</sup> In 2002, Aldridge reported spectroscopic data for the cyclopentadienyl complex  $[\text{Fe}(\text{BCl}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  ( $\delta_{\text{B}}$  90.7),<sup>10</sup> originally described by Nöth and Schmid,<sup>3</sup> obtained from the reaction between  $\text{BCl}_3$  and  $\text{Na}[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ . This was followed by a theoretical study on a range of similar metal boryl complexes, including  $\text{BF}_2$  and  $\text{BCl}_2$  examples, designed to probe the nature of the metal–boron bond.<sup>11</sup> More recently, Braunschweig and

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co-workers have presented structural data for  $[\text{Fe}(\text{BCl}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  ( $\delta_{\text{B}}$  90.0), the first dichloroboryl complex to be structurally characterised.<sup>12</sup> These authors also reported the structure of the 4-picoline adduct  $[\text{Fe}\{\text{BCl}_2(4\text{-pic})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  ( $\delta_{\text{B}}$  18.8) in which the nitrogen atom is directly bonded to the boron centre.<sup>12</sup> In later reports, Braunschweig and co-workers have described the analogous pentamethylcyclopentadienyl complexes  $[\text{Fe}(\text{BCl}_2)(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$  ( $\delta_{\text{B}}$  94.9)<sup>13</sup> and  $[\text{Fe}(\text{BBr}_2)(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$  ( $\delta_{\text{B}}$  94),<sup>14</sup> the former affording, on reaction with  $[\text{Pd}(\text{PCy}_3)_2]$ , the heteronuclear complex  $[(\eta\text{-C}_5\text{Me}_5)\text{Fe}(\mu\text{-CO})_2(\mu\text{-BCl}_2)\text{Pd}(\text{PCy}_3)]$  ( $\delta_{\text{B}}$  72.2) containing a bridging dichloroboryl ligand.<sup>13</sup> Spectroscopic data were also presented for the phosphine adduct  $[\text{Fe}\{\text{BCl}_2(\text{PCy}_3)\}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$  ( $\delta_{\text{B}}$  3.4).<sup>13</sup> Both the cyclopentadienyl and pentamethylcyclopentadienyl iron dichloroboryl compounds have also been employed as precursors in the synthesis of dinuclear species containing substituent-free bridging boron atoms.<sup>15</sup>

In most of the recent studies, and much of the early work reported by Nöth and Schmid, the dihaloboryl species were prepared from a reaction between a boron trihalide and an anionic transition metal complex. The exceptions to this method involved an oxidative addition reaction either of a B–B bond, in the case of the  $\text{BF}_2$  complexes,<sup>6</sup> or of a boron–halogen bond in the case of some of the platinum and cobalt complexes described by Nöth and Schmid.<sup>3</sup> In view of the known facile oxidative addition of B–X bonds to  $\text{Pt}(0)$ , exemplified by the synthesis of such compounds as  $[\text{PtCl}\{\text{B}(\text{cat})\}(\text{PPh}_3)_2]$ ,<sup>16</sup>  $[\text{PtCl}\{\text{BCl}(\text{NMe}_2)\}(\text{PPh}_3)_2]$ <sup>17</sup> and  $[\text{PtBr}\{\text{BBr}(\text{Fc})\}(\text{PCy}_3)_2]$  ( $\text{Fc}$  = ferrocenyl;  $\text{Cy}$  = cyclohexyl)<sup>18</sup> from  $\text{ClB}(\text{cat})$ , 1,2- $\text{B}_2\text{Cl}_2(\text{NMe}_2)_2$  and  $\text{BBr}_2(\text{Fc})$  respectively, we were interested in establishing whether dihaloboryl compounds could be accessed directly from  $\text{Pt}(0)$  precursors and boron trihalides. Herein we describe the results of those studies.

## Results and discussion

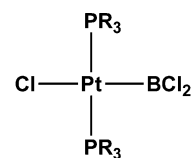
We were not the first to examine the reactions between phosphine– $\text{Pt}(0)$  complexes and boron trihalides. Indeed, the reaction between  $\text{BBr}_3$  and  $[\text{Pt}(\text{PPh}_3)_4]$  in cyclohexane, reported by Nöth, Schmid and co-workers<sup>3,4</sup> and mentioned above in the Introduction, was purported to give the  $\text{Pt}(\text{II})$  complex  $[\text{PtBr}(\text{BBr}_2)(\text{PPh}_3)_2]$ . However, in subsequent work by Durkin and Schram<sup>19</sup> and later Wallbridge and co-workers,<sup>20</sup> compounds formulated as Lewis acid–base adducts were described. Thus Durkin and Schram reported that treatment of solid  $[\text{Pt}(\text{PPh}_3)_3]$  with gaseous  $\text{BCl}_3$  afforded the 1 : 2 adduct  $(\text{Ph}_3\text{P})_3\text{Pt}\cdot 2\text{BCl}_3$ , the same species being formed, along with  $\text{Ph}_3\text{P}\cdot\text{BCl}_3$ , when  $[\text{Pt}(\text{PPh}_3)_4]$  was employed.<sup>19</sup> This 1 : 2 adduct was apparently unstable with respect to ligand dissociation when dissolved in a solvent and when the reaction between  $[\text{Pt}(\text{PPh}_3)_3]$  and  $\text{BCl}_3$  was carried out in benzene solution, a product formulated as  $(\text{Ph}_3\text{P})\text{Pt}\cdot\text{BCl}_3$  was proposed. In the later work by Wallbridge and co-workers,<sup>20</sup> the reaction between either  $[\text{Pt}(\text{PPh}_3)_4]$  or  $[\text{Pt}(\text{PPh}_3)_2(\eta\text{-C}_2\text{H}_4)]$  and  $\text{BF}_3$  in toluene was reported to afford the adduct  $(\text{Ph}_3\text{P})_2\text{Pt}\cdot 2\text{BF}_3$  which was shown to react with  $\text{BCl}_3$  to give  $(\text{Ph}_3\text{P})_2\text{Pt}\cdot 2\text{BCl}_3$ .

In this study, the reaction between  $[\text{Pt}(\text{PMe}_3)_4]$  (prepared *in situ* from  $[\text{Pt}(\text{nbe})_2]$  ( $\text{nbe}$  = norbornene) and four equivalents of  $\text{PMe}_3$ ), and four equivalents of  $\text{BCl}_3$  in toluene afforded the phosphine adduct  $\text{Me}_3\text{PBCl}_3$  ( $\delta_{\text{B}}$  0.86,  $^1J_{\text{PB}}$  164.7) and a platinum boryl species formulated as  $[\text{PtCl}(\text{BCl}_2)(\text{PMe}_3)_2]$  (**1**), the  $^{11}\text{B}$  NMR chemical shift and well resolved coupling to platinum being consistent

with the presence of a  $\text{BCl}_2$  ligand ( $\delta_{\text{B}}$  62.2,  $^1J_{\text{PtB}}$  1214 Hz;  $\delta_{\text{P}}$  –14.6,  $^1J_{\text{PtP}}$  2635 Hz). Attempts to crystallise **1** from this reaction mixture were unsuccessful, resulting only in small quantities of the species  $[\text{PtCl}(\text{PMe}_3)_3][\text{BCl}_4]$ , although isolated yields of **1** as a white powder were typically >90%.  $[\text{PtCl}(\text{PMe}_3)_3][\text{BCl}_4]$  was characterised by X-ray crystallography, details for which are given in Table 1.

Similar reactions employing the phosphines  $\text{PPh}_3$ ,  $\text{PMePh}_2$ ,  $\text{PMe}_2\text{Ph}$  and  $\text{PCy}_3$  ( $\text{Cy}$  = cyclohexyl) were also carried out. For  $\text{PPh}_3$  and  $\text{PMePh}_2$  the adducts  $\text{Ph}_3\text{PBCl}_3$  and  $\text{Ph}_2\text{MePBCl}_3$  were formed (the former characterised crystallographically) in addition to boryl products identified spectroscopically as  $[\text{PtCl}(\text{BCl}_2)(\text{PPh}_3)_2]$  (**2**) [ $\delta_{\text{B}}$  59(br);  $\delta_{\text{P}}$  23.0,  $^1J_{\text{PtP}}$  3023 Hz] and  $[\text{PtCl}(\text{BCl}_2)(\text{PMePh}_2)_2]$  (**3**) [ $\delta_{\text{B}}$  61(br);  $\delta_{\text{P}}$  7.6,  $^1J_{\text{PtP}}$  2890 Hz] although in both these cases, the boryl signals in the  $^{11}\text{B}$  NMR were broad and no coupling to platinum was resolved. Attempted crystallisation of **2** and **3** resulted only in the complexes  $[\text{PtCl}(\text{PPh}_3)_3][\text{BCl}_4]$  and  $[\text{Pt}_2(\mu\text{-Cl})_2(\text{PMePh}_2)_4][\text{BCl}_4]_2$ ; the latter characterised by X-ray crystallography, details for which are given in Table 1. No spectroscopic evidence was observed for platinum boryl complexes when reactions involving the phosphines  $\text{PMe}_2\text{Ph}$  and  $\text{PCy}_3$  were carried out, the only isolated products being  $\text{PhMe}_2\text{PBCl}_3$  and  $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$  respectively, both identified by X-ray crystallography.

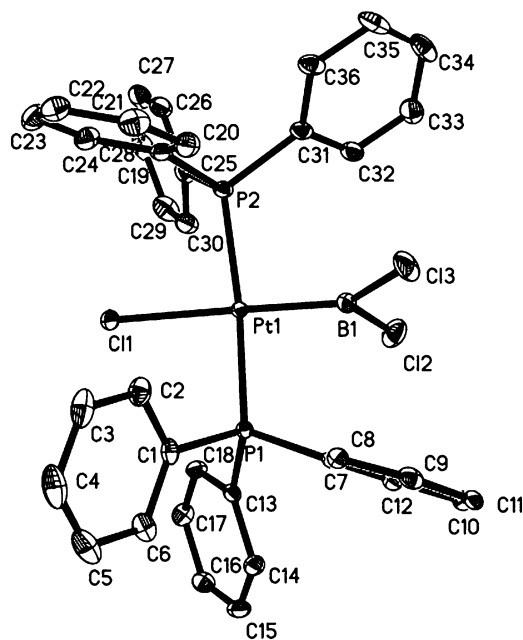
In all of the reactions carried out above, it was the tetraphosphine  $\text{Pt}(0)$  species, generated *in situ*, which was employed as the platinum starting material and  $\text{BCl}_3$  was added in the molar ratio 4B : 1Pt. These reactions were attempted in light of some of the earlier studies referenced above but whilst they afforded the desired dichloroboryl species in some cases, the products were difficult to isolate not least because of the presence of the co-formed phosphine– $\text{BCl}_3$  adducts. Reactions were therefore carried out in which only two equivalents of phosphine were added to the  $\text{Pt}(0)$  species  $[\text{Pt}(\text{nbe})_2]$  followed by one equivalent of  $\text{BCl}_3$ . Thus reaction between  $[\text{Pt}(\text{nbe})_2]$ , two equivalents of the phosphines  $\text{PPh}_3$ ,  $\text{PMePh}_2$  or  $\text{PMe}_2\text{Ph}$  and one equivalent of  $\text{BCl}_3$  afforded, in each case, high yields of the dichloroboryl species **2**, **3** and  $[\text{PtCl}(\text{BCl}_2)(\text{PMe}_2\text{Ph})_2]$  (**4**) [ $\delta_{\text{B}}$  = 61.8 (br);  $\delta_{\text{P}}$  –6.7,  $^1J_{\text{PtP}}$  2731 Hz]. However, under similar conditions using  $\text{PMe}_3$ , although  $^{31}\text{P}$  NMR spectroscopy showed the presence of **1**, the solutions decomposed rapidly to platinum metal. When an excess of  $\text{BCl}_3$  was used, the unusual dinuclear species **5** was formed (see below).



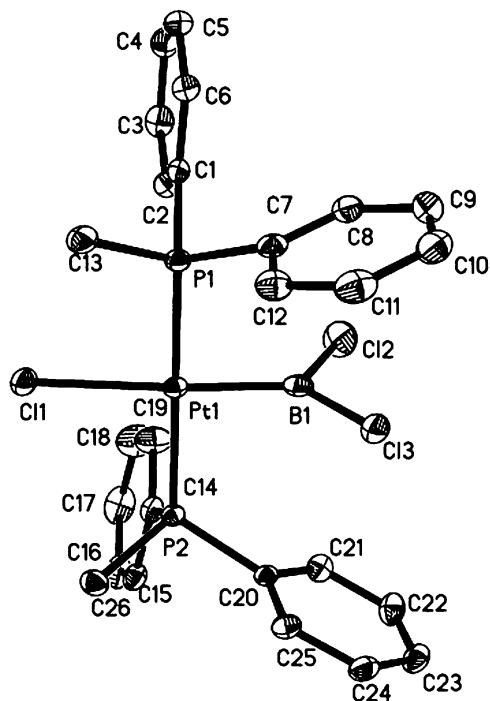
**2**, R = Ph; **3**, R<sub>3</sub> = Ph<sub>2</sub>Me; **4**, R<sub>3</sub> = PhMe<sub>2</sub>

The complexes **2**, **3** and **4** were characterised by X-ray crystallography, the results for which are shown in Fig. 1–3; crystallographic data for all complexes are presented in Table 1. All three molecules (two per asymmetric unit for **4**) adopt similar structures in the solid state in which the boryl group is *trans* to the chloride, consistent with the known high *trans* influence of boryl ligands.<sup>1,21</sup> The Pt–B bond distances (**2**, 1.972(3); **3**, 1.988(3); **4**, 1.963(6), 1.971(6) Å) are all similar but markedly shorter than the Pt–B distance in *trans*- $[\text{PtCl}\{\text{B}(\text{cat})\}(\text{PPh}_3)_2]$  (2.008(8) Å)<sup>16</sup> although the

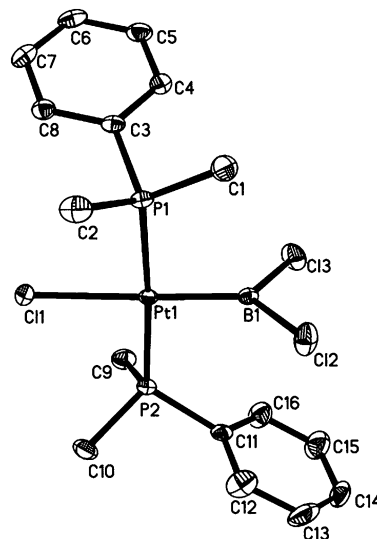




**Fig. 1** A view of the molecular structure of compound **2**. Selected bond length (Å) and angle (°) data include: Pt(1)–B(1) 1.972(3), Pt(1)–Cl(1) 2.4368(8), Pt(1)–P(1) 2.3005(7), Pt(1)–P(2) 2.2950(7), B(1)–Cl(2) 1.791(3), B(1)–Cl(3) 1.779(3); Cl(1)–Pt(1)–B(1) 173.03(8), P(1)–Pt(1)–P(2) 169.45(2), Cl(2)–B(1)–Cl(3) 113.12(4), Pt(1)–B(1)–Cl(2) 119.85(14), Pt(1)–B(1)–Cl(3) 127.03(15); interplanar angle 81.0.



**Fig. 2** A view of the molecular structure of compound **3**. Selected bond length (Å) and angle (°) data include: Pt(1)–B(1) 1.988(3), Pt(1)–Cl(1) 2.4461(8), Pt(1)–P(1) 2.2961(9), Pt(1)–P(2) 2.3005(9), B(1)–Cl(2) 1.789(3), B(1)–Cl(3) 1.757(3); Cl(1)–Pt(1)–B(1) 173.25(9), P(1)–Pt(1)–P(2) 173.51(2), Cl(2)–B(1)–Cl(3) 113.57(18), Pt(1)–B(1)–Cl(2) 119.16(18), Pt(1)–B(1)–Cl(3) 127.27(17); interplanar angle 92.7.



**Fig. 3** A view of the molecular structure of compound **4**. Selected bond length (Å) and angle (°) data include: Molecule 1 Pt(1)–B(1) 1.963(6), Pt(1)–Cl(1) 2.4385(15), Pt(1)–P(1) 2.3065(15), Pt(1)–P(2) 2.3003(15), B(1)–Cl(2) 1.794(7), B(1)–Cl(3) 1.778(7); Cl(1)–Pt(1)–B(1) 176.8(2), P(1)–Pt(1)–P(2) 176.22(5), Cl(2)–B(1)–Cl(3) 111.2(3), Pt(1)–B(1)–Cl(2) 124.9(4), Pt(1)–B(1)–Cl(3) 123.9(4); interplanar angle 85.8. Molecule 2 Pt(2)–B(2) 1.971(6), Pt(2)–Cl(4) 2.4433(15), Pt(2)–P(3) 2.3017(15), Pt(2)–P(4) 2.2994(15), B(2)–Cl(5) 1.780(7), B(2)–Cl(6) 1.782(7); Cl(4)–Pt(2)–B(2) 173.3(2), P(3)–Pt(2)–P(4) 175.46(5), Cl(5)–B(2)–Cl(6) 111.4(3), Pt(2)–B(2)–Cl(5) 125.1(4), Pt(2)–B(2)–Cl(6) 123.5(4); interplanar angle 92.8.

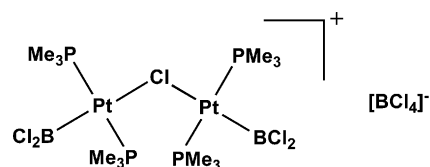
Pt–Cl distances are more comparable (**2**, 2.4368(8); **3**, 2.4461(8); **4**, 2.4385(15), 2.4433(15); [PtCl{B(cat)}(PPh<sub>3</sub>)<sub>2</sub>] 2.4446(14) Å).<sup>16</sup> In the complex *trans*-[PtCl{BCl(NMe<sub>2</sub>)}(PPh<sub>3</sub>)<sub>2</sub>],<sup>17</sup> the Pt–B and Pt–Cl distances are 2.075(10) and 2.470(2) Å, respectively, revealing that the Pt–B bond length is broadly correlated with the expected Lewis acidity of the boryl group, *i.e.* shorter for a more Lewis acidic boron. Each boron centre in **2**, **3** and **4** is trigonal planar, the Cl–B–Cl angle being a little less than 120° and the two Pt–B–Cl angles being slightly greater (the slight asymmetry in **2** and **3** is not present in **4**); a similar set of angles is observed for [Fe(BCl<sub>2</sub>)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)].<sup>12</sup> In all cases, the angle between the mean platinum square plane and the mean boron trigonal plane is close to 90° (**2**, 81.0; **3**, 92.7; **4**, 85.8, 92.8°) which compares with the corresponding angles for [PtCl{B(cat)}(PPh<sub>3</sub>)<sub>2</sub>] (78.3°)<sup>16</sup> and [PtCl{BCl(NMe<sub>2</sub>)}(PPh<sub>3</sub>)<sub>2</sub>] (90.0°).<sup>17</sup> We note a recent report from Marder and co-workers<sup>21</sup> describing DFT studies on Pt(II) boryl species of the type [PtCl(BR<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>]. The trends observed experimentally in the Pt–B and Pt–Cl bond lengths are in full accord with those predicted by the DFT calculations. Thus the *trans* influence of the B(cat) and BCl<sub>2</sub> groups was calculated to be nearly identical, whilst shorter Pt–B distances were anticipated for Pt–BCl<sub>2</sub> (1.976 Å) *vs.* Pt–B(cat) (2.005 Å).<sup>21</sup>

Reactions involving the diphosphines dppe (1,2-bis(diphenylphosphino)ethane) and dppm (bis(diphenylphosphino)methane) were also carried out. Thus reaction between [Pt<sub>2</sub>(dppm)<sub>3</sub>] and BCl<sub>3</sub> afforded a mixture of products, one of which was shown by X-ray crystallography to be the dppm–BCl<sub>3</sub> adduct Cl<sub>3</sub>BP(Ph)<sub>2</sub>CH<sub>2</sub>(Ph)<sub>2</sub>PBCl<sub>3</sub>, details of which are given in Table 1.

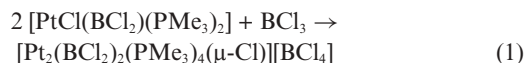


Crystals of the unusual dinuclear species  $[\text{Pt}_2(\text{BCl}_2)_2(\text{PMe}_3)_4(\mu\text{-Cl})][\text{BCl}_4]^-$  (**5**) were obtained. A view of the structure of the cation is shown in Fig. 4 which reveals an arrangement in which two square planar platinum(II) centres are linked by a single bridging chloride which is *trans* to a  $\text{BCl}_2$  group on each platinum centre. Both Pt–B bonds [1.960(5) and 1.955(4) Å] are similar in length to those observed for **2**, **3** and **4** as are the Pt–Cl bond lengths [2.5155(10) and 2.5088(11) Å]; the boron trigonal planes are also close to orthogonal with respect to the platinum square planes (89.4 and

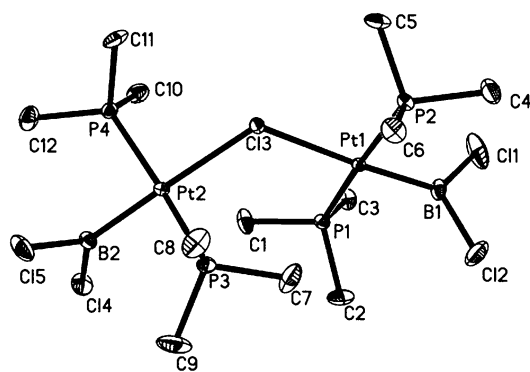
86.3°). Whilst the mechanism by which compound **5** is formed is unclear, a formal equation for its formation, eqn (1), is consistent with the expected high *trans* influence of the boryl groups resulting in the lability of a *trans* chloride which is subsequently scavenged by  $\text{BCl}_3$ .



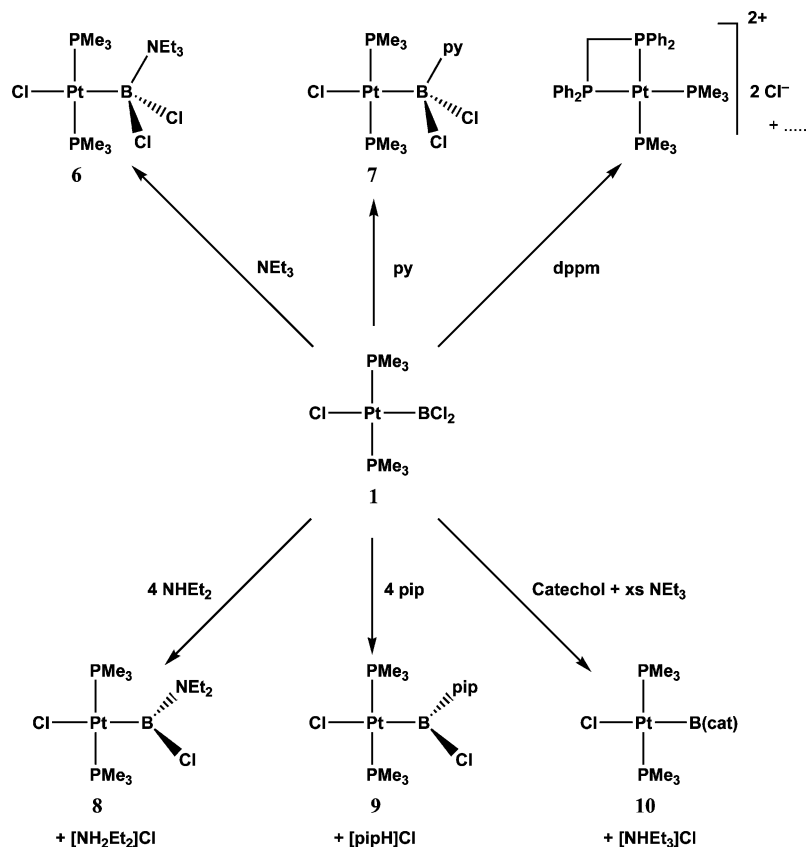
**5**



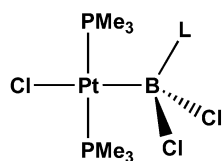
Having a reliable route to quantities of  $[\text{PtCl}(\text{BCl}_2)(\text{PMe}_3)_2]$  (**1**), enabled a study of its reactivity to be carried out which is summarised in Scheme 1. Thus treatment of **1** with  $\text{NEt}_3$  or pyridine (py) afforded the adducts  $[\text{PtCl}\{\text{BCl}_2(\text{NEt}_3)\}(\text{PMe}_3)_2]$  (**6**) ( $\delta_{\text{B}}$  27.8;  $\delta_{\text{P}}$  –13.0,  $^1J_{\text{PtP}}$  2643 Hz) and  $[\text{PtCl}\{\text{BCl}_2(\text{py})\}(\text{PMe}_3)_2]$  (**7**) ( $\delta_{\text{B}}$  29.9,  $^1J_{\text{PtB}}$  957;  $\delta_{\text{P}}$  –10.4,  $^1J_{\text{PtP}}$  2694 Hz) respectively, both characterised spectroscopically. Proposed structures for **6** and **7** are shown in the diagrams below consistent both with the  $^{11}\text{B}$  NMR data and the known structure of the species  $[\text{Fe}\{\text{BCl}_2(4\text{-pic})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ .<sup>12</sup> Treatment of **1** with dpmm afforded a mixture of products of which only the salt  $[\text{Pt}(\text{PMe}_3)_2(\text{dpmm})]\text{Cl}_2$  was characterised; X-ray crystallographic data for this species are given in the Experimental section.



**Fig. 4** A view of the molecular structure of compound **5**. Selected bond length (Å) and angle (°) data include: Pt(1)–B(1) 1.960(5), Pt(2)–B(2) 1.955(4), Pt(1)–Cl(3) 2.5155(10), Pt(2)–Cl(3) 2.5088(11), B(1)–Cl(1) 1.759(5), B(1)–Cl(2) 1.778(5), B(2)–Cl(4) 1.780(5), B(2)–Cl(5) 1.771(5); B(1)–Pt(1)–Cl(3) 175.54(13), P(1)–Pt(1)–P(2) 176.11(4), B(2)–Pt(2)–Cl(3) 171.40(13), P(3)–Pt(2)–P(4) 168.70(4), Pt(1)–Cl(3)–Pt(2) 126.48(4); interplanar angles 89.4 [B(1)] and 86.3 [B(2)].

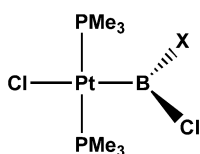


**Scheme 1**



6, L = NEt<sub>2</sub>; 7, L = py

The reaction between **1** and either four equivalents of NEt<sub>2</sub> or piperidine (pipH) resulted in the mono-substituted boryl species *trans*-[PtCl{BCl(NEt<sub>2</sub>)}(PMe<sub>3</sub>)<sub>2</sub>] (**8**) ( $\delta_B$  35.9,  $^1J_{PtB}$  1028;  $\delta_P$  13.1,  $^1J_{PtP}$  2772 Hz) and [PtCl{BCl(pip)}(PMe<sub>3</sub>)<sub>2</sub>] (**9**) ( $\delta_B$  34.3;  $\delta_P$  -9.9,  $^1J_{PtP}$  3000 Hz) respectively, the eliminated HCl in each case removed as [NH<sub>2</sub>Et<sub>2</sub>]Cl or [pipH<sub>2</sub>]Cl. Even with sufficient diethylamine or piperidine present, no evidence was obtained for a disubstituted boryl species. Spectroscopic data for **8** and **9** were consistent with the proposed structures and compound **8** was also characterised by X-ray crystallography, the results of which are shown in Fig. 5. The structure of **8** is similar to those of **2**, **3** and **4** described above. Notable differences, however, are the longer Pt–B and Pt–Cl bond lengths [2.005(4) and 2.4604(10) Å respectively], the former a likely consequence of the less Lewis acidic boron centre resulting from the  $\pi$ -donor diethylamido substituent as described earlier. The angle between the platinum mean square plane and the boron mean trigonal plane is 90.0° and that between the adjacent boron and nitrogen trigonal planes is 6.0° (consistent with the  $\pi$ -donor properties of the amido nitrogen). In all respects, the structure of **8** is similar to that previously reported for the dimethylamido analogue *trans*-[PtCl{BCl(NMe<sub>2</sub>)}(PPh<sub>3</sub>)<sub>2</sub>].<sup>17</sup>



8, X = NEt<sub>2</sub>; 9, X = pip

Treatment of either **1** (in the presence of excess NEt<sub>3</sub>) or **8** with catechol afforded the B(cat) derivative *trans*-[PtCl{B(cat)}(PMe<sub>3</sub>)<sub>2</sub>] (**10**) (Schemes 1 and 2) characterised spectroscopically ( $\delta_B$  33.3,  $^1J_{PtB}$  1039;  $\delta_P$  -12.6,  $^1J_{PtP}$  2768 Hz) and by

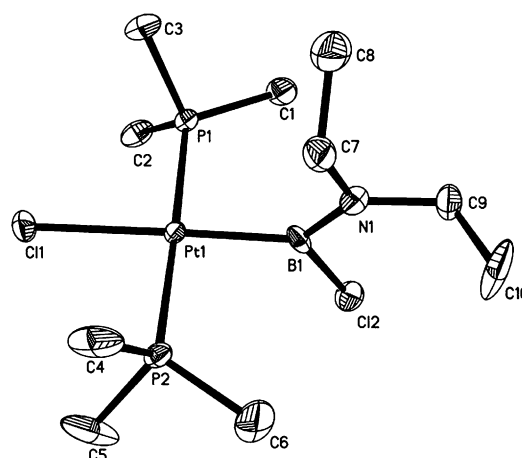
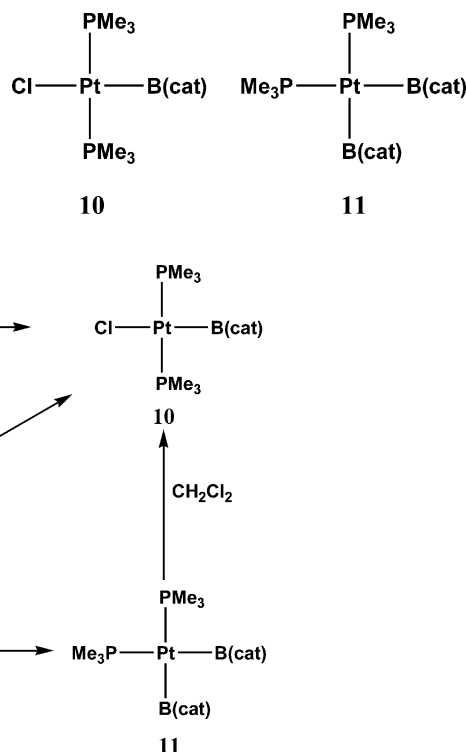
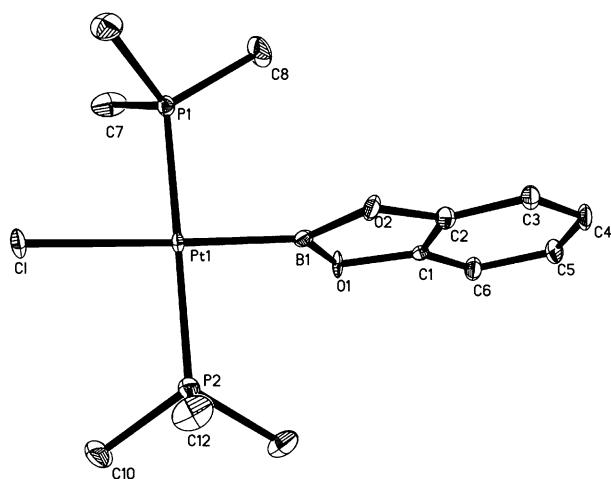


Fig. 5 A view of the molecular structure of compound **8**. Selected bond length (Å) and angle (°) data include: Pt(1)–B(1) 2.005(4), Pt(1)–Cl(1) 2.4604(10), Pt(1)–P(1) 2.2835(10), Pt(1)–P(2) 2.2795(10), B(1)–Cl(2) 1.843(5), B(1)–N(1) 1.394(6); Cl(1)–Pt(1)–B(1) 178.86(15), P(1)–Pt(1)–P(2) 178.33(4), Cl(2)–B(1)–N(1) 115.5(3), Pt(1)–B(1)–Cl(2) 117.1(2), Pt(1)–B(1)–N(1) 127.4(3); interplanar angle 90.0.

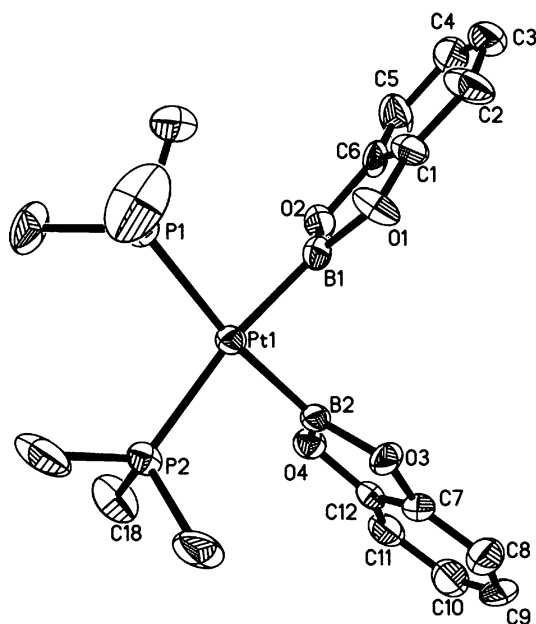
X-ray crystallography. The results of the structure determination are shown in Fig. 6 and reveal the expected *trans* geometry as observed for related species including the chloro–B(cat) complex *trans*-[PtCl{B(cat)}(PPh<sub>3</sub>)<sub>2</sub>].<sup>16</sup> As shown in Scheme 2, complex **10** was formed in the reaction between [Pt(PMe<sub>3</sub>)<sub>4</sub>] and ClB(cat) and also from the slow decomposition of *cis*-[Pt{B(cat)}<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] (**11**) in dichloromethane over a period of months. Compound **11** ( $\delta_B$  49.4;  $\delta_P$  -14.3,  $^1J_{PtP}$  1490 Hz) was prepared from the reaction between [Pt(PMe<sub>3</sub>)<sub>4</sub>] and B<sub>2</sub>(cat)<sub>2</sub>, by analogy with other Pt(II) bis-boryl species,<sup>1,16,17,22</sup> and is structurally similar (Fig. 7) to all related bis-phosphine, platinum(II) bis-boryl species.<sup>1,16,17,22</sup>



Scheme 2



**Fig. 6** A view of the molecular structure of compound **10**. Selected bond length (Å) and angle (°) data include: Pt(1)–B(1) 1.995(6), Pt(1)–Cl(1) 2.4308(16), Pt(1)–P(1) 2.284(2), Pt(1)–P(2) 2.289(2), B(1)–O(1) 1.423(7), B(1)–O(2) 1.415(7); Cl(1)–Pt(1)–B(1) 178.15(18), P(1)–Pt(1)–P(2) 178.48(5), O(1)–B(1)–O(2) 108.8(5), Pt(1)–B(1)–O(1) 124.2(4), Pt(1)–B(1)–O(2) 127.0(4); interplanar angle 95.8.



**Fig. 7** A view of the molecular structure of compound **11**. Selected bond length (Å) and angle (°) data include: Pt(1)–B(1) 2.061(10), Pt(1)–B(2) 2.032(9), Pt(1)–P(1) 2.331(2), Pt(1)–P(2) 2.327(2), B(1)–O(1) 1.413(12), B(1)–O(2) 1.388(14), B(2)–O(3) 1.415(11), B(2)–O(4) 1.413(11); B(1)–Pt(1)–B(2) 82.2(2), P(1)–Pt(1)–P(2) 101.47(8), O(1)–B(1)–O(2) 108.1(7), Pt(1)–B(1)–O(1) 126.7(7), Pt(1)–B(1)–O(2) 124.6(7), O(3)–B(2)–O(4) 107.8(7), Pt(1)–B(2)–O(3) 128.6(7), Pt(1)–B(2)–O(4) 123.5(6); interplanar angles 81.4 [B(1)], 91.5 [B(2)].

In conclusion, these studies have shown that platinum(II) dichloroboryl complexes of the form *trans*-[PtCl(BCl<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub>] can be formed in high yield from the oxidative addition of a B–Cl bond in BCl<sub>3</sub> to a platinum(0) centre in the presence of two equivalents of a phosphine ligand. Furthermore, an examination of the reactivity of such species, *trans*-[PtCl(BCl<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>] in particular, reveals an adduct chemistry associated with the Lewis acidic boron

centre, consistent with the previous work of Braunschweig,<sup>12</sup> and a substitution chemistry of the B–Cl bond(s) which parallels the chemistry observed by Roper for the related osmium BCl<sub>2</sub> complex described in the Introduction.<sup>8,9</sup> The original report by Nöth and Schmid of oxidative addition of BBr<sub>3</sub> to Pt(0) resulting in a BBr<sub>2</sub> ligand is therefore consistent with these studies. In contrast, however, we obtained no evidence for BCl<sub>3</sub> adducts of platinum(0) as described by Schram<sup>19</sup> and later Wallbridge.<sup>20</sup>

## Experimental

### General procedures

All reactions were performed under dry dinitrogen using standard Schlenk line techniques. Dry solvents were obtained from an anhydrous engineering system and were degassed prior to use. All reagents were procured commercially and used without further purification except for [Pt(nbe)<sub>3</sub>]<sup>23</sup> (nbe = norbornene = bicyclo[2.2.1]heptene) and B<sub>2</sub>(cat)<sub>2</sub><sup>24</sup> which were prepared by literature methods.

### Preparations

**[PtCl(BCl<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>] (1).** [Pt(nbe)<sub>3</sub>] (0.10 g, 0.21 mmol) was dissolved in hexane (5 cm<sup>3</sup>), to which PMe<sub>3</sub> (0.099 cm<sup>3</sup>, 0.84 mmol) was added through a micro-syringe. The reaction mixture was stirred for 1 h, and the solvent was removed *in vacuo* to give a white solid. The solid was redissolved in toluene (10 cm<sup>3</sup>), and BCl<sub>3</sub> (0.84 cm<sup>3</sup>, 0.84 mmol, 1 M in heptane) was added at –78 °C. The mixture was allowed to warm to room temperature, and stirred for 1 h during which time a quantity of white precipitate formed. After this time, all volatiles were removed *in vacuo*, and the solid was redissolved in toluene (10 cm<sup>3</sup>) and filtered, affording a colourless solution which was allowed to stand overnight resulting in a further precipitate of the by-product, Me<sub>3</sub>PBCl<sub>3</sub>. The solvent was removed slowly *in vacuo*, and the resulting solid redissolved in toluene (5 cm<sup>3</sup>), and filtered to produce a solution of **1** from which a white powder was obtained after further solvent removal (0.096 g, 97%). Spectroscopic data for **1**: NMR (C<sub>6</sub>D<sub>6</sub>) <sup>1</sup>H{<sup>1</sup>H} δ 62.2 (<sup>1</sup>J<sub>PtB</sub> 1214 Hz), <sup>31</sup>P{<sup>1</sup>H} δ –14.6 (<sup>1</sup>J<sub>PtP</sub> 2635 Hz); <sup>1</sup>H δ 1.12 (m), <sup>13</sup>C{<sup>1</sup>H} δ 13.9 (t, <sup>1</sup>J<sub>PC</sub> 20 Hz); mass spectrum (EI) 383 (M<sup>+</sup> – BCl<sub>2</sub>). Attempts to crystallise **1** from this reaction mixture were unsuccessful, resulting only in small quantities of the species identified as [PtCl(PMe<sub>3</sub>)<sub>3</sub>][BCl<sub>4</sub>] by X-ray crystallography.

**[PtCl(BCl<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (2).** [Pt(nbe)<sub>3</sub>] (0.20 g, 0.42 mmol) and PPh<sub>3</sub> (0.22 g, 0.84 mmol) were dissolved in toluene (5 cm<sup>3</sup>) and the reaction mixture stirred for 1 h, after which time the solvent was removed *in vacuo* to give a white solid. This solid was then dissolved in toluene (5 cm<sup>3</sup>), and BCl<sub>3</sub> (0.42 cm<sup>3</sup>, 0.42 mmol, 1 M in heptane) was added at –78 °C. The mixture was allowed to warm to room temperature, and stirred for 1 h during which time a white precipitate formed. All volatiles were then removed *in vacuo*, and the resulting solid washed with toluene (3 × 1 cm<sup>3</sup>) (0.29 g, 81%). Colourless crystals suitable for X-ray crystallography were formed from solutions in toluene (1 cm<sup>3</sup>) and CH<sub>2</sub>Cl<sub>2</sub> (1 cm<sup>3</sup>) layered with hexane. Spectroscopic data for **2**: NMR (C<sub>6</sub>D<sub>6</sub>) <sup>1</sup>H{<sup>1</sup>H} δ 59 (br), <sup>31</sup>P{<sup>1</sup>H} δ 23.0 (<sup>1</sup>J<sub>PtP</sub> 3023 Hz), <sup>1</sup>H δ 7.66–7.73 (m), 7.33–7.41 (m), <sup>13</sup>C{<sup>1</sup>H} δ 140.0 (s), 134.9 (t, J<sub>PC</sub> 6.0), 130.6 (s), 128.3 (t,

$J_{\text{PC}}$  4.5); mass spectrum (EI) 754 ( $\text{M}^+ - \text{BCl}_2$ ). Anal. Calcd for  $\text{C}_{36}\text{H}_{30}\text{BCl}_3\text{P}_2\text{Pt}$ : H, 3.60; C, 51.65%. Found H, 3.70; C, 51.60%.

**[PtCl(BCl<sub>2</sub>)(PMePh<sub>2</sub>)<sub>2</sub>] (3).** [Pt(nbe)<sub>3</sub>] (0.10 g, 0.21 mmol) and PMePh<sub>2</sub> (0.080 cm<sup>3</sup>, 0.42 mmol) were dissolved in toluene (5 cm<sup>3</sup>) and the reaction mixture was stirred for 1 h, after which time the solvent was removed *in vacuo* to give an off-white oil. This oil was then dissolved in toluene (5 cm<sup>3</sup>), and BCl<sub>3</sub> (0.21 cm<sup>3</sup>, 0.21 mmol, 1 M in heptane) was added at  $-78^\circ\text{C}$ . The mixture was allowed to warm to room temperature, and stirred for 1 h. All volatiles were then removed *in vacuo*, and the resulting solid was redissolved in toluene (3 cm<sup>3</sup>) and filtered. The filtrate was evaporated *in vacuo* to give a white solid (0.085 g, 57%). Colourless crystals suitable for X-ray crystallography were formed from solutions in toluene (1 cm<sup>3</sup>) layered with hexane. Spectroscopic data for **3**: NMR ( $\text{C}_6\text{D}_6$ )  $^{11}\text{B}\{^1\text{H}\}$   $\delta$  61 (br),  $^{31}\text{P}\{^1\text{H}\}$   $\delta$  7.6 ( $^1J_{\text{PIP}}$  2890 Hz); mass spectrum (EI) 631 ( $\text{M}^+ - \text{BCl}_2$ ).

**[PtCl(BCl<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (4).** [Pt(nbe)<sub>3</sub>] (0.10 g, 0.21 mmol) and PMe<sub>2</sub>Ph (0.061 cm<sup>3</sup>, 0.42 mmol) were dissolved in toluene (5 cm<sup>3</sup>) and the reaction mixture stirred for 1 h, after which time the solvent was removed *in vacuo* to give an off-white oil. This oil was then dissolved in toluene (5 cm<sup>3</sup>), and BCl<sub>3</sub> (0.21 cm<sup>3</sup>, 0.21 mmol, 1 M in heptane) was added at  $-78^\circ\text{C}$ . The mixture was allowed to warm to room temperature, and stirred for 1 h. All volatiles were then removed *in vacuo*, and the resulting solid was redissolved in toluene (3 cm<sup>3</sup>) and filtered. The filtrate was evaporated *in vacuo* to give a white solid (0.087 g, 74%). Colourless crystals suitable for X-ray crystallography were formed from solutions in toluene (1 cm<sup>3</sup>) layered with hexane. Spectroscopic data for **4**: NMR ( $\text{C}_6\text{D}_6$ )  $^{11}\text{B}\{^1\text{H}\}$   $\delta$  61.8 (br),  $^{31}\text{P}\{^1\text{H}\}$   $\delta$   $-6.7$  ( $^1J_{\text{PIP}}$  2731 Hz),  $^1\text{H}$   $\delta$  7.58–7.65 (m), 7.00–7.08 (m), 1.56 (t,  $^3J_{\text{PH}}$  18.0,  $^2J_{\text{PH}}$  3.0 Hz),  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  131.3 (t,  $J_{\text{PC}}$  6.0), 130.1 (s), 128.4 (t,  $J_{\text{PC}}$  5.3), 13.3 (t,  $J_{\text{PC}}$  19.6); mass spectrum (EI) 507 ( $\text{M}^+ - \text{BCl}_2$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{BCl}_3\text{P}_2\text{Pt}$ : H, 3.75; C, 32.65%. Found H, 3.85; C, 32.75%.

**[Pt<sub>2</sub>(BCl<sub>2</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>( $\mu$ -Cl)][BCl<sub>4</sub>] (5).** [Pt(nbe)<sub>3</sub>] (0.10 g, 0.21 mmol) was dissolved in hexane (5 cm<sup>3</sup>), to which PMe<sub>3</sub> (0.055 cm<sup>3</sup>, 0.42 mmol) was added through a micro-syringe. The reaction mixture was stirred for 1 h, and all the volatiles were removed *in vacuo* to give an off-white oil. The solid was redissolved in toluene (5 cm<sup>3</sup>), and an excess of BCl<sub>3</sub> (0.4 cm<sup>3</sup>, 0.46 mmol, 1 M in heptane) was added at  $-78^\circ\text{C}$ . The mixture was allowed to warm to room temperature, and stirred for 1 h during which time a quantity of black oil formed. After this time, all volatiles were removed *in vacuo*, and the solid was redissolved in toluene (10 cm<sup>3</sup>) and filtered, affording a colourless solution. The solvent was removed slowly *in vacuo* to give a white powder (0.047 g, 43%). Colourless crystals suitable for X-ray crystallography were formed from solutions in toluene (1 cm<sup>3</sup>) layered with hexane. Spectroscopic data for **5**: NMR ( $\text{C}_6\text{D}_6$ )  $^{11}\text{B}\{^1\text{H}\}$   $\delta$  60.6 ( $^1J_{\text{PIB}}$  1242 Hz), 11.1 (s),  $^{31}\text{P}\{^1\text{H}\}$   $\delta$   $-14.7$  ( $^1J_{\text{PIP}}$  2628 Hz),  $^1\text{H}$   $\delta$  1.08 (t,  $^3J_{\text{PH}}$  18.0,  $^2J_{\text{PH}}$  3.0 Hz),  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  14.0 (t,  $J_{\text{PC}}$  19.6 Hz); mass spectrum (EI) 383 ( $\text{M}^+ - \text{Pt}(\text{BCl}_2)_2$ ). Anal. Calcd for  $\text{C}_{12}\text{H}_{36}\text{B}_3\text{Cl}_9\text{P}_4\text{Pt}_2$ : H, 3.45; C, 13.80%. Found H, 3.40; C, 13.80%.

**[PtCl{BCl<sub>2</sub>(NEt<sub>3</sub>)}(PMe<sub>3</sub>)<sub>2</sub>] (6).** A sample of compound **1** (0.10 g, 0.21 mmol) was dissolved in toluene (5 cm<sup>3</sup>), to which an

excess of NEt<sub>3</sub> (0.5 cm<sup>3</sup>) was then added. The mixture was stirred overnight affording a white precipitate of compound **6** (0.043 g, 36.9%). Spectroscopic data for **6**: NMR ( $\text{CD}_3\text{CN}$ )  $^{11}\text{B}\{^1\text{H}\}$   $\delta$  27.8 (br),  $^{31}\text{P}\{^1\text{H}\}$   $\delta$   $-13.0$  ( $^1J_{\text{PIP}}$  2643 Hz),  $^1\text{H}$   $\delta$  3.58–3.65 (q), 1.88 (t), 1.21 (br).

**[PtCl{BCl<sub>2</sub>(py)}(PMe<sub>3</sub>)<sub>2</sub>] (7).** A sample of compound **1** (0.10 g, 0.21 mmol) was dissolved in toluene (5 cm<sup>3</sup>) and the solution was layered with an excess of pyridine (3 cm<sup>3</sup>). After one week, a white precipitate of compound **7** was obtained which was washed with hexane (3  $\times$  2 cm<sup>3</sup>) (0.052 g, 46.5%). Spectroscopic data for **7**: NMR ( $\text{CD}_3\text{CN}$ )  $^{11}\text{B}\{^1\text{H}\}$   $\delta$  29.9 ( $^1J_{\text{PIB}}$  957 Hz),  $^{31}\text{P}\{^1\text{H}\}$   $\delta$   $-10.4$  ( $^1J_{\text{PIP}}$  2694 Hz). Both **6** and **7** are prone to loss of the Lewis base bound to boron which prevented more extensive spectroscopic and analytical characterisation.

**[PtCl{BCl(NEt<sub>2</sub>)}(PMe<sub>3</sub>)<sub>2</sub>] (8).** A sample of compound **1** (0.10 g, 0.21 mmol) was dissolved in toluene (10 cm<sup>3</sup>), to which HNEt<sub>2</sub> (0.085 cm<sup>3</sup>, 0.84 mmol) was added. After stirring for 2 h, the solution became cloudy and a white precipitate formed. The solution was filtered and allowed to stand overnight affording a precipitate of [NH<sub>2</sub>Me<sub>2</sub>]Cl. After filtration and removal of the solvent, compound **8** was obtained as a white solid (0.095 g, 91.7%). Colourless crystals suitable for X-ray crystallography were formed from solutions in toluene (0.5 cm<sup>3</sup>) layered with hexane. Spectroscopic data for **8**: NMR ( $\text{C}_6\text{D}_6$ )  $^{11}\text{B}\{^1\text{H}\}$   $\delta$  35.9 ( $^1J_{\text{PIB}}$  1028 Hz),  $^{31}\text{P}\{^1\text{H}\}$   $\delta$   $-13.1$  ( $^1J_{\text{PIP}}$  2772 Hz),  $^1\text{H}$   $\delta$  3.41–3.35 (q, 2H); 3.24–3.19 (q, 2H); 1.26 (t, 6H,  $^3J_{\text{PH}}$  12.0,  $^2J_{\text{PH}}$  3.0 Hz); 0.95 (t, 3H); 0.88 (t, 3H),  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  47.5 ( $\text{CH}_2$ ,  $^3J_{\text{PC}}$  70.4 Hz), 41.3 ( $\text{CH}_2$ ,  $^3J_{\text{PC}}$  22.1 Hz), 14.7 (s,  $\text{CH}_3$ ), 14.5 (m,  $^1J_{\text{PC}}$  19.1,  $^2J_{\text{PC}}$  38.2 Hz); mass spectrum (EI) 465 ( $\text{M}^+ - \text{Cl}$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_{28}\text{BCl}_2\text{NP}_2\text{Pt}$ : H, 5.65; C, 23.95%. Found H, 5.60; C, 24.00%.

**[PtCl{BCl(pip)}(PMe<sub>3</sub>)<sub>2</sub>] (9).** A sample of compound **1** (0.10 g, 0.21 mmol) was dissolved in toluene (10 cm<sup>3</sup>), to which piperidine (0.081 cm<sup>3</sup>, 0.84 mmol) was added. After stirring for 2 h, the solution became cloudy and a white precipitate formed. The solution was filtered and allowed to stand affording a precipitate of [pipH<sub>2</sub>]Cl. After filtration and removal of the solvent, compound **9** was obtained as a white solid (0.083 g, 78.3%). Spectroscopic data for **9**: NMR ( $\text{C}_6\text{D}_6$ )  $^{11}\text{B}\{^1\text{H}\}$   $\delta$  34.3 (br),  $^{31}\text{P}\{^1\text{H}\}$   $\delta$   $-9.9$  ( $^1J_{\text{PIP}}$  3000 Hz). Despite the similarity to compound **8**, which has been fully characterised, satisfactory analytical data were not obtained for **9**.

**[PtCl{B(cat)}(PMe<sub>3</sub>)<sub>2</sub>] (10).** A sample of compound **1** (0.10 g, 0.21 mmol) was dissolved in toluene (5 cm<sup>3</sup>), and an excess of NEt<sub>3</sub> (0.5 cm<sup>3</sup>) was added followed by a solution of catechol (0.023 g, 0.21 mmol) in toluene (5 cm<sup>3</sup>). The mixture was stirred for 2 h at room temperature affording compound **10** as a white solid (0.076 g, 72%). Spectroscopic data for **10**: NMR ( $\text{CH}_3\text{CN}$ )  $^{11}\text{B}\{^1\text{H}\}$   $\delta$  33.3 ( $^1J_{\text{PIB}}$  1039 Hz),  $^{31}\text{P}\{^1\text{H}\}$   $\delta$   $-12.6$  ( $^1J_{\text{PIP}}$  2768 Hz),  $^1\text{H}$   $\delta$  7.15–7.25 (m,  $\text{C}_6\text{H}_4$ ), 6.85–6.90 (m,  $\text{C}_6\text{H}_4$ ), 1.14 (m,  $\text{CH}_3$ ),  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  149.9 (s,  $\text{C}_6\text{H}_4$ ), 121.7 (s,  $\text{C}_6\text{H}_4$ ), 111.4 (s,  $\text{C}_6\text{H}_4$ ), 14.8 (t,  $\text{CH}_3$ ,  $^1J_{\text{PC}}$  20.1); mass spectrum (EI) 383 ( $\text{M}^+ - \text{Bcat}$ ). Anal. Calcd for  $\text{C}_{12}\text{H}_{22}\text{BClO}_2\text{P}_2\text{Pt}$ : H, 4.40; C, 28.75%. Found H, 4.30; C, 28.70%. Compound **10** was also prepared, although not isolated, by the following methods and identified spectroscopically ( $^{11}\text{B}$  and  $^{31}\text{P}$  NMR).



**Method (i).** A sample of compound **8** (0.10 g, 0.19 mmol) was dissolved in toluene (5 cm<sup>3</sup>) to which a solution of catechol (0.063 g, 0.57 mmol) in toluene (5 cm<sup>3</sup>) was added.

**Method (ii).** A sample of compound **11** (0.11 g, 0.18 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) and the solution allowed to stand for 2 months. After this time, colourless crystals of **10** were obtained by layered the solution with hexane.

**Method (iii).** A sample of [Pt(PMe<sub>3</sub>)<sub>4</sub>] (0.11 g, 0.21 mmol) was dissolved in toluene (5 cm<sup>3</sup>) to which a solution of ClB(cat) (32 mg, 0.21 mmol) in toluene (5 cm<sup>3</sup>) was added.

**[Pt{B(cat)}<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] (**11**).** A sample of [Pt(nbe)<sub>3</sub>] (0.10 g, 0.21 mmol) was dissolved in hexane (5 cm<sup>3</sup>), to which PMe<sub>3</sub> (0.099 cm<sup>3</sup>, 0.84 mmol) was added through a micro-syringe. The reaction mixture was stirred for 1 h at room temperature and the solvent removed *in vacuo* affording a white solid. This solid was dissolved in toluene (10 cm<sup>3</sup>), and B<sub>2</sub>(cat)<sub>2</sub> (0.05 g, 0.21 mmol) was added. The resulting mixture was stirred for 2 h at room temperature to give white precipitate. The solvent volume to was reduced to 1.5 cm<sup>3</sup> *in vacuo* and the white precipitate was filtered off, washed with toluene (2 cm<sup>3</sup>) and hexane (2 × 2 cm<sup>3</sup>) and dried *in vacuo* (0.081 g, 65%). Colourless crystals suitable for X-ray crystallography were formed from solutions in CH<sub>2</sub>Cl<sub>2</sub> (1 cm<sup>3</sup>) layered with hexane. Spectroscopic data for **11**: NMR (CD<sub>2</sub>Cl<sub>2</sub>) <sup>1</sup>H{<sup>1</sup>H} δ 49.4 (br), <sup>31</sup>P{<sup>1</sup>H} δ -14.3 (<sup>1</sup>J<sub>PP</sub> 1490 Hz), <sup>1</sup>H δ 7.13–7.07 (m, C<sub>6</sub>H<sub>4</sub>, 4H), 6.91–6.86 (m, C<sub>6</sub>H<sub>4</sub>, 4H), 1.50 (br, CH<sub>3</sub>, 18H), <sup>13</sup>C{<sup>1</sup>H} δ 149.9 (s, C<sub>6</sub>H<sub>4</sub>), 120.8 (s, C<sub>6</sub>H<sub>4</sub>), 111.4 (s, C<sub>6</sub>H<sub>4</sub>), 19.2 (t, CH<sub>3</sub>, <sup>1</sup>J<sub>PC</sub> 12.1); mass spectrum (EI) 346 (M<sup>+</sup> – 2Bcat). Anal. Calcd for C<sub>18</sub>H<sub>26</sub>B<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Pt: H, 4.50; C, 36.95%, Found H, 4.40; C, 37.00%.

## X-Ray crystallography

Crystallographic data for compounds Ph<sub>3</sub>BCl<sub>3</sub>, PhMe<sub>2</sub>PBCl<sub>3</sub>, **3**, **4** and Cl<sub>3</sub>BP(Ph)<sub>2</sub>CH<sub>2</sub>(Ph)<sub>2</sub>PBCl<sub>3</sub>, were collected at 173 K on a Bruker-AXS SMART 1K diffractometer using Mo-Kα radiation (λ = 0.71073 Å). For compounds [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>][BCl<sub>4</sub>]<sub>2</sub>, [Pt<sub>2</sub>Cl<sub>2</sub>(μ-Cl)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>], **2** and **8**, data were collected at 100 K on a Bruker-AXS SMART Apex diffractometer equipped with monochromated beam focussing optics using Mo-Kα radiation (λ = 0.71073 Å). For compounds [PtCl(PMe<sub>3</sub>)<sub>3</sub>][BCl<sub>4</sub>], **10** and **11**, data were collected using Cu-Kα radiation (λ = 1.5418 Å) at 100 K on a Bruker-AXS Proteum diffractometer equipped with a rotating anode source operated at 4.8 kW and Osmic CMF12-38Cu6 (blue) mirror optics. For all compounds, intensity data were collected as a series of frames, each of ω width 0.3°, integrated<sup>25</sup> and corrected for absorption<sup>26</sup> and solved and refined using routine techniques.<sup>27</sup> The symmetrically unique anion in complex [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>][BCl<sub>4</sub>]<sub>2</sub> shows positional disorder for three of its chlorine atoms. A sensible model for this disorder was obtained by restraining the sets of Cl...Cl distances in each of the disordered components to be equal and restraining the displacement parameters of pairs of chlorine atoms opposite each other with respect to the undistorted B(1)–Cl(2) axis to be equal. Attempts to find a satisfactory model for the solvent present in the structure of [Pt(PMe<sub>3</sub>)<sub>2</sub>(dppm)]Cl<sub>2</sub> were unsuccessful and a diffuse solvent correction was applied to the intensity data of this compound using the SQUEEZE program of the Platon software suite.<sup>28</sup> The Flack parameter for [PtCl(PMe<sub>3</sub>)<sub>3</sub>][BCl<sub>4</sub>] indicates that

this crystal may be a racemic twin. Crystallographic data for all compounds are presented in Table 1.

CCDC reference numbers 618539–618552.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612039n

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